



Comparison of various digestion procedures in chemical analysis of spent hydrodesulfurization catalyst

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ABSTRACT

Four digestion procedures have been tested to verify their applicability to the determination of major and trace elements (Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sr, Ti, V, Zn) in a spent catalyst by inductively coupled plasma optical emission spectrometry (ICP-OES). Two digestion procedures have been carried out in a closed microwave system using: (1) HCl + HNO₃ + H₂O₂; (2) HNO₃ + HF, whereas the remaining two in an open system using: (1) aqua regia + NH₄F, HNO₃, H₂SO₄; (2) HF + HClO₄, H₃BO₃, HCl. Among these four procedures the microwave digestion system (1) gave the best recovery results. The quality of the analytical results has been evaluated by the analysis of the CTA-FFA-1 Fine Fly Ash Certified Reference Material. A good agreement between the measured and reference values was found for almost all elements. The precision was assessed from the replicate analyses of microwave digestion (1) system and was found to be less than 5% of the relative standard deviation (R.S.D.).

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1. Introduction

Catalysts based on valuable metals such as nickel, cobalt and molybdenum are commonly used in the oil industry, especially for the hydrodesulfurization of petroleum fractions. This process, however, results in production of spent catalysts comprising such elements as: S, C, V, Fe, Ni, Si and traces of As, P [1,2]. Spent catalysts are classified as hazardous materials. To avoid pollution they are subjected to metal extraction [3,4]. On the other hand, the recovery of metals from those catalysts can be also an important source of limited metals.

The digestion of catalyst samples is an indispensable step before the determination of metal concentrations. It can be a critical point in the analysis since the incompleteness in the process and element losses occur what causes significant errors during the examination of elements. Classically, the digestion of samples is carried out on a hot-plate with different combinations of mineral acids [5–8] such as HNO₃, HNO₃ + HCl, HNO₃ + HCl + HF, HNO₃ + HF, HNO₃ + HClO₄, etc., and alkali fusion [9,10] with Na₂CO₃, Na₂CO₃ + Na₂B₄O₇, LiBO₂ and Li₂B₄O₇. The conventional acid digestion procedures are time consuming, require use of hazardous acids and often lead to systematic errors and failures. In the last few years closed microwave oven systems [5,6,8,11–14] have been developed. Such a microwave digestion system has been investigated in an attempt to improve

the yield of extracted metal, to reduce the process time and to use small volumes of reagents.

The validation of digestion methods is necessary to assure reliable results. One way to assess accuracy of the method is the analysis of the certified reference materials. A reference material can be really useful if the matrix is similar to the analyzed sample and the concentrations of the analyzed elements are comparable. A major challenge in quantifying metal emission from refineries is the lack of a certified material for hydrodesulfurization catalysts. There are no exact literature data about such material nor at least about substances having similar properties. There is also no information about reference materials detailing the content of the metals. This is mainly due to the fact that the data on the catalyst's composition are confidential.

Various methods have been presented to digest materials with the matrix similar to the samples investigated by us (sewage sludge, fly ash, petroleum products and different catalysts).

Kowalewska et al. [15] studied the determination of Cu in a wide range of petroleum products from a crude oil distillation using flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), and inductively coupled plasma mass spectrometry (ICP-MS). Different procedures of a sample preparation were evaluated. The best one for these materials seems to be the mineralization in an open system with sulfuric acid.

Mester et al. [16] compared microwave decomposition methods and a wet acid digestion in the solubilization of Cr, Ni, Cu, Pb, Cd and Zn, for their determination in fly ash. The microwave

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methods included different combinations of concentrated mineral acids, such as: (1) HNO₃, (2) HNO₃, HF and H₃BO₃, (3) HNO₃, HF, H₃BO₃ with addition of H₂O₂, (4) HNO₃, HF, HF and H₃BO₃ (5) HNO₃, HF, HClO₄ and H₃BO₃. For the conventional wet procedure *aqua regia* with hydrochloric acid were applied.

In turn, determination of Cd, Cu, Ni, As and Pb in coal fly ash by ICP-MS was studied by Xie et al. [17]. It was shown that the optimal conditions of the process were obtained using close microwave digestion with HNO₃, HClO₄ and HF.

Recchia et al. [18] have used different digestion methods to determine platinum in Pt-Sn/MgO catalysts by ETAAS. The used digestion procedures included: open-vessel digestion with concentrated hydrochloric acid, Bunsen flame digestion, hotplate and microwave digestion with the used *aqua regia*. The analytical results indicated that the microwave digestion allowed the recovery of metal up to 100% for the catalyst analyzed, and demonstrated significantly better precision than other digestion methods.

The studies published by Kulkarni et al. [19] focused on two microwave-assisted acid digestion procedures with (1) nitric acid and (2) nitric acid, hydrofluoric acid and boric acid, applied for the analysis of 27 non-rare earth elements, as well as several rare earth elements (Y, La, Ce, Pr, Nd, Tb, Dy, Er) in a fluidized-bed catalytic cracking (FCC) catalyst. They found that the second tested method was successfully implemented to quantitatively measurements.

The main purpose of the present work was to compare and evaluate various digestion procedures in application to a spent hydrodesulfurization catalyst. Fifteen elements (Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sr, Ti, V, Zn) were measured with the use of inductively coupled plasma optical emission spectrometry (ICP-OES) detection method. The effectiveness of the applied classical and microwave methods was assessed and discussed. Certified Reference Material was used for verification of digestion procedures and measurements of elements.

2. Experimental

2.1. Apparatus

The concentrations of elements (Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sr, Ti, V, Zn) in digests were measured by atomic emission spectrometry with inductively coupled argon plasma as the excitation source. The Jobin-Yvon 38S spectrometer was equipped with a Meinhard nebuliser and a cyclonic chamber. The operating parameters and analytical line wavelengths used are shown in Table 1. Before the analysis all the solutions were filtered through a hard filter paper. The resulting solutions were diluted to the required concentration range needed for further analysis.

2.2. Reagents and standard solutions

All reagents used in this study were of analytical grade. For sample digestion, concentrated HNO₃ and HCl (Merck KGaA, Darmstadt, Germany), 40% HF, 60% HClO₄, 99.5% H₃BO₃, and 98% H₂SO₄ (POCh S.A., Gliwice, Poland) were applied. With each set of digested samples a blank sample was simultaneously prepared through the complete procedure, analyzed and then used for correction of the analytical signals. Working standard solutions were prepared by suitable dilution of the ICP multi-element standard solution (1000 µg mL⁻¹, supplied by Merck). Both dissolution and all dilutions were performed with deionised water with a specific resistance of 18.3 MΩ cm⁻¹ obtained from EASYpure™ (Baenstead, Thermolyne Corporation, USA). Glassware were cleaned with 10% nitric acid in ultrasonic bath (for 30 min) and rinsed several times with deionised water.

Table 1
Instrumental and operating conditions for ICP-OES

Discharge parameters			
Forward power		1000 W	
Frequency		40.68 MHz	
Plasma gas flow rate		15 L min ⁻¹	
Sheath gas flow rate		0.2 L min ⁻¹	
Nebuliser gas flow rate		0.3 L min ⁻¹	
Sample uptake		0.75 mL min ⁻¹	
Monochromator			
		1 m Czerny-Turner	
		Type: HR 1000	
Gratings		4320 and 2400 grooves mm ⁻¹	
Slit width (entrance/exit)		20 µm/50 µm	
Photomultiplier			
		R 955	
Plasma observation zone		Radial, 12 mm above load coil	
Analytical lines (wavelengths in nm)			
Al (I)	396.152	Mo (I)	202.030
Ba (II)	233.527	Ni (II)	231.604
Cd (II)	228.802	Pb (II)	221.647
Co (II)	238.892	Sr (II)	407.771
Cr (II)	267.716	Ti (I)	334.941
Cu (I)	324.754	V (II)	292.402
Fe (II)	259.940	Zn (I)	213.856
Mn (II)	259.373		

I: atomic; II: ionic lines.

2.3. Sample

The spent Ni-Mo/Al₂O₃ catalyst used for reducing sulfur in petroleum products was in the form of cylindrical extrudates of approximate diameter 0.3–0.4 mm and length 4–6 mm. It contained residual oil and was washed with hot toluene by Soxhlet process, dried at 110 °C and homogenized by mixing before experiments. The surface of the deoiled catalyst has been determined by nitrogen adsorption (BET method) as 80.0 m² g⁻¹. Powder XRD analysis of the spent catalyst showed that its main phase is γ-Al₂O₃, but V₅S₈ compound was also detected. In turn, CHNS analysis showed that the spent catalyst contained (wt%) carbon 17.6, hydrogen 1.14, nitrogen 0.38 and sulfur 9.64. TEM analysis confirmed the existence of γ-Al₂O₃, Ni₃S₄ and V₅S₈, as well as revealed molybdenum sulfide (MoS₂). All metal sulfide deposits on a hydrodesulfurization catalyst are crystallites of 10–30 nm. SEM-EDX analysis has shown that metal foulants such as vanadium, nickel and iron are concentrated near the outer surface of the catalyst extrudate, blocking the pore mouths and retarding the access of the reactants to the active sites of the catalyst with the pores [20].

2.4. Digestion procedures

Four different procedures were applied in order to digest the catalyst sample. The analytical performance digestion procedures were evaluated using CTA-FFA-1 Fine Fly Ash Certified Reference Material.

2.4.1. Conventional hot-plate digestion procedures (CD)

2.4.1.1. Procedure 1 (CD1). Approximately 0.1 g of powdered catalyst was transferred into 150 mL Teflon beakers and 3 mL of *aqua regia* were added. The sample was slowly heated to the acid evaporation. Subsequently, to the cool solution, 0.300 g of ammonium fluoride and 1 mL of concentrated nitric acid were added and the solution was again heated for 10 min. After cooling 1.5 mL of diluted (1:1) sulfuric acid (VI) was added to the Teflon beakers and the solution was heated once more until white fumes stop to evaporate. To the cool beaker content 10 mL deionised water were poured

Table 2
Applied microwave programme for digestion of reference materials and the spent catalyst

Step	Power (W)	Time (min)
1	250	4
2	0	5
3	250	6
4	400	5
5	0	5
6	500	10
7	0	5

in and the sample was heated until sulfates dissolution. Insoluble residue was filtered off through the hard filter paper and several times rinsed with hot distilled water acidified with sulfuric acid (VI). At the end the beakers content was quantitatively transferred into the 100 mL volumetric flask and filled up with deionised water.

2.4.1.2. Procedure 2 (CD2). To the Teflon beakers, containing powdered catalyst moistened with water, 3 mL of concentrated hydrofluoric acid and 2 mL of concentrated perchloric acid were added. Next, the Teflon beakers content was heated on a hot-plate until the solution was evaporated almost to dryness. Then, 4 mL of 3% boric acid was added to the hot solution in the beakers to complex with any free hydrofluoric acid and the vessel with its content was heated once again. Almost dry residue was dissolved in 4 mL of concentrated hydrochloric acid. After the cooling the sample solution was quantitatively transferred into a volumetric flask and made up to the 100 mL with deionised water.

2.4.2. Microwave-assisted digestion procedures (MD)

The high-pressure microwave sample decomposition was performed using Milestone digestion system (MLS-1200 MEGA) equipped with a rotor (MDR 300/10).

2.4.2.1. Procedure 3 (MD1). About 0.1 g of powdered material was accurately weighted into a Teflon digestion vessel. Then 3 mL of concentrated hydrochloric acid, 7 mL of concentrated nitric acid and 3 mL of hydrogen peroxide (30%) were added. On the next day decomposition of the sample was carried out in a microwave digestion system. The sample was subjected to the microwave heating with maximum power of 500 W for 35 min. Details of the microwave heating programme are listed in Table 2. After the cooling the sample solution was quantitatively transferred into 100 mL volumetric flask and made up to the volume with deionised water.

2.4.2.2. Procedure 4 (MD2). An aliquot (0.1 g) of sample was placed into a digestion Teflon vessel. Concentrated nitric (5 mL) and hydrofluoric (1 mL) acids were added. The sample was digested applying the microwave heating programme given in Table 2. It was completed in 40 min including 5 min of ventilation. After the digestion process the digests were diluted up with deionised water up to 100 mL.

3. Results and discussion

3.1. Digestion procedures

In this work, different digestion methods for the analysis of total elements content in a hydrodesulfurization catalyst were investigated. Using multi-elemental standard solutions for calibration, concentrations of Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sr, Ti, V and Zn were simultaneously measured in the solutions obtained using two conventional and two microwave-assisted digestion methods.

During all the measurements the argon line Ar I (356.766 nm) was monitored to control the stability of plasma excitation conditions.

Total concentrations of the elements determined in the analyzed hydrodesulfurization catalyst are shown as arithmetic means and standard deviations in Table 3.

The comparable efficiency of digestion with all applied procedures were obtained for Co, Cr, Mo, Ni and V. For these elements the lowest standard deviation values were observed in the solutions obtained with microwave method 3 (MD1). In the case of Ni, this value was insignificantly higher than others. The compatible results were also obtained for Al and Fe in the solution applying methods 1 and 3, as well as for Ba and Mn with methods 3 and 4. The results of these elements determination were much lower in the remaining two methods. Concentration of Zn determined in solutions obtained after application of method 3 was comparable. For elements such as Sr (methods 1) and Ti (method 3), the highest leaching efficiency was achieved. The lowest mineralization efficiency was obtained for Al, Cd and Fe concentrations measured in the solutions achieved with method 2. These values significantly differed from those gained with all the other methods. Concentrations of Sr in a digest obtained by methods 2 (CD2) and 4 (MD2) are below a detection limit. None of the examined catalyst dissolution methods lead to a detectable amount of Pb leaching. Procedure 1 (CD1) was not suitable for Ba determination. The use of the microwave-assisted procedure (method 4—MD2) was not sufficient to gain measurable Ti concentrations. In the case of procedure 3 (MD1) accurate results were obtained for all metals investigated, except calcium and lead.

The highest value of the standard deviation was observed for Cd, Cu, Fe and Sr after digestion by method 1; Ba, Mn and Zn by method 4; Ti by method 2; Co and Cr (methods 2 and 4) and Mo (methods 1 and 4). The most precise results (i.e. the standard deviations below 5%) were gained for the majority of elements (Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Sr, Ti) with the digestion procedure 3.

The precision metals determination in the hydrodesulfurization catalyst after mineralization in a closed system with nitric acid, hydrochloric acid and hydrogen peroxide (MD1) (expressed as relative standard deviation (R.S.D.) for the all determinations) remains at the level of a few percent, varying from 0.60% (Ti, V) to 4.7% (Sr). In the case of method 1 (CD1) for elements such as Al, Co, Fe, Mo, Ni, V and Zn, the R.S.D. values were below 5%. For methods 2 and 3, only for Ba, Co, Mo, Mn, Ni and V, a high precision (<5%) was obtained. These data are demonstrated in Table 4.

During the digestion procedure using methods CD2 and MD2 it was found that the decomposition was not complete or not reproducible for some samples. On the basis of the results shown in Table 3, procedure 3 microwave digestion with HCl + HNO₃ + H₂O₂ was chosen as the most effective catalysts digestion method. This technique provided a better solubilization of the matrix, increasing reproducibility between different replicates and satisfactory precision (relative standard deviation at the level of a few percent—see Table 4).

The comparison of the elements measurement in the hydrodesulfurization catalyst obtained by different digestion methods was made using *t*-test [21]. The results are shown in Table 5 with the significance level notation (S or NS). As can be seen, procedure 1 (conventional with mixture *aqua regia* + NH₄F, HNO₃, H₂SO₄) and procedure 4 (microwave digestion with HNO₃ + HF) can be used alternatively instead of method 3 (microwave using HCl + HNO₃ + H₂O₂), however only in application to the selected elements. Procedure 2 (conventional digestion—HF + HClO₄, H₃BO₃, HCl) was found to be not suitable for proper determination of examined elements and could lead to analytical errors during analysis of the catalyst samples.

Table 3
Analytical results for the hydrodesulfurization catalyst using different digestion methods ($n=5$)

Element	Concentration ^a			
	Procedure 1 (CD1) Aqua regia, NH ₄ F, HNO ₃ , H ₂ SO ₄	Procedure 2 (CD2) HF, HClO ₄ , H ₃ BO ₃ , HCl	Procedure 3 (MD1) HCl, HNO ₃ , H ₂ O ₂	Procedure 4 (MD2) HNO ₃ , HF
Al ⁺	9.63 ± 0.11	2.84 ± 0.52	10.11 ± 0.06	0.357 ± 0.20
Ba	<DL	60.9 ± 3.0	93.8 ± 1.4	89.1 ± 3.3
Cd	3.22 ± 1.00	3.01 ± 0.03	3.61 ± 0.01	1.74 ± 0.20
Co	31.8 ± 1.4	32.3 ± 1.6	33.9 ± 1.2	34.3 ± 1.5
Cr	9.67 ± 0.50	10.1 ± 1.2	10.7 ± 0.5	9.39 ± 1.23
Cu	18.2 ± 3.2	18.6 ± 1.2	15.3 ± 0.1	15.5 ± 1.2
Fe	653 ± 26	545 ± 12	685 ± 17	140 ± 9
Mn	66.1 ± 3.4	90.2 ± 1.4	104 ± 1	101 ± 4
Mo [*]	3.08 ± 0.13	3.11 ± 0.06	3.36 ± 0.02	3.43 ± 0.11
Ni ⁺	1.62 ± 0.03	1.52 ± 0.03	1.67 ± 0.05	1.70 ± 0.04
Pb	<DL	<DL	<DL	<DL
Sr	15.3 ± 2.4	<DL	6.79 ± 0.32	<DL
Ti	28.3 ± 1.9	29.0 ± 2.3	38.4 ± 0.2	<DL
V ⁺	5.71 ± 0.26	5.78 ± 0.20	5.96 ± 0.03	5.98 ± 0.17
Zn	102 ± 5	82.6 ± 4.5	101 ± 1	108 ± 7

DL—detection limits.

^a Mean values ± S.D. ($\mu\text{g g}^{-1}$) except (*) as wt%.**Table 4**
Values of relative standard deviation (%) for tested digestion procedures

Element	Method 1 Aqua regia, NH ₄ F, HNO ₃ , H ₂ SO ₄	Method 2 HF, HClO ₄ , H ₃ BO ₃ , HCl	Method 3 HCl, HNO ₃ , H ₂ O ₂	Method 4 HNO ₃ , HF
Al	1.14	18.3	0.60	56.0
Ba	–	4.93	1.50	3.70
Cd	31.0	1.0	0.28	11.5
Co	4.40	4.95	3.54	4.37
Cr	5.17	11.9	4.67	13.1
Cu	17.6	6.50	0.65	7.74
Fe	3.98	2.20	2.48	6.43
Mn	5.14	1.60	0.96	3.96
Mo	4.22	1.93	0.60	3.21
Ni	1.85	1.97	3.00	2.35
Pb	–	–	–	–
Sr	15.7	–	4.70	–
Ti	6.70	8.00	0.52	–
V	4.55	3.46	0.50	2.84
Zn	4.90	5.50	1.00	6.50

The results with R.S.D. higher than 5% are indicated by italics.

3.2. Verification of the measurement accuracy

As no certified reference material for the hydrodesulfurization catalyst was available, the Certified Reference Material (CTA-FFA-1

Table 5
Results of t -test between method 3 and the others

Element	Method 1 Aqua regia, NH ₄ F, HNO ₃ , H ₂ SO ₄ Significance ^a	Method 2 HF, HClO ₄ , H ₃ BO ₃ , HCl Significance ^a	Method 4 HNO ₃ , HF Significance ^a
Al	S	S	S
Ba	–	S	S
Cd	NS	S	S
Co	NS	NS	NS
Cr	NS	NS	NS
Cu	S	S	NS
Fe	S	S	S
Mn	S	S	NS
Mo	NS	S	NS
Ni	NS	S	NS
Pb	–	–	–
Sr	S	–	–
Ti	S	S	–
V	NS	NS	NS
Zn	NS	S	NS

^a Significance of t -test ($n=5$) at 95% confidence level.

Fine Fly Ash, Institute of Nuclear Chemistry and Technology, Poland) was used to validate the preparation procedure and the accuracy of the determination method. This reference material was expected to have the chemical composition similar to the analyzed sample. Concentration of elements was measured in samples mineralized by mixture nitric acid, hydrochloric acid and hydrogen peroxide in a closed system with the aid of microwave energy (methods MD1). The t -test was used to find out whether a statistically significant difference occurred between the means of the found and certified values at 95% confidence level. The results of this test and of the measurements are shown with the significance level notation (S or NS) in Table 6. The concentrations are expressed as $\mu\text{g g}^{-1}$ (excepted Al, Mo, Ni and V given by wt%) and the values are the mean of five independent determinations. For most of the examined elements a good agreement between obtained data and the certified values is observed. For Al, Ba, Cd, Cr, Fe, Mn, Ni, Pb, Sr, Ti and Zn the differences in concentrations (measured and certified) were found to be within the limits of standard deviation uncertainties. In addition, the t -test also showed that no statistically significant difference occurred between the means of both values for these elements. This was denoted by NS in Table 6. On the other hand, the average concentrations of Co, Cu and V were far from the certified values. For Cu and V the obtained values were lower than certified (Cu 27%, V 37%), and higher than certified for Co (about

Table 6
Accuracy check level of procedure 3—MD1 with CTA-FFA-1 Fine Fly Ash

Element	Concentration ^a		Value of <i>t</i> -test	Significance ^c
	Certified value	Experimental data		
Al ⁺	14.87 ± 0.39	14.3 ± 0.9	1.49	NS
Ba	835 ± 56	856 ± 23	2.04	NS
Cd	2.8 ^b	2.64 ± 0.13	2.75	NS
Co	39.8 ± 1.7	51.2 ± 1.2	21.2	S
Cr	156 ± 8	142 ± 12	2.61	NS
Cu	158 ± 9	116 ± 7	13.4	S
Fe ⁺	4.89 ± 0.14	4.73 ± 0.15	2.38	NS
Mn	1066 ± 41	1033 ± 28	2.63	NS
Mo ⁺	17 ^b	<DL	–	–
Ni	99.0 ± 5.8	97.9 ± 2.83	0.87	NS
Pb	369 ± 46	332 ± 30	2.75	NS
Sr	250 ± 13	249 ± 6	0.37	NS
Ti ⁺	0.58 ^b	0.57 ± 0.03	2.23	NS
V	260 ± 10	164 ± 7	30.7	S
Zn	569 ± 58	525 ± 37	2.72	NS

DL—detection limit.

^a Mean values ± S.D. ($\mu\text{g g}^{-1}$) except (*) as wt%.

^b Information value.

^c Significance of *t*-test ($n = 5$) at 95% confidence level.

29%). High recovery (129%) for Co is due to the great complexity of the dissolved matrix, which can affect the recovery of some minor elements. Furthermore, the *t*-test indicated that there was a statistically significant difference between the measured concentrations and the certified values for the elements Co, Cu and V. This was indicated by S in Table 6 as well. For Ca, Cd, Mo and Ti the certified reference material producer gave only information values. In the case of Mo the concentration was below a detection limit.

4. Conclusion

Digestion of a hydrodesulfurization catalyst using HCl + HNO₃ + H₂O₂ in a microwave system (procedure 3) was chosen as the most effective method. For nearly all determined metals the results are sufficiently accurate and precise. This method provided a better solubilization of the matrix, increasing reproducibility between different replicates and satisfactory precision. Procedure 1 and 4 can be alternatively used instead of method 3, however only in application to the selected elements. Procedure 2 was found to be not suitable for a proper determination of examined elements and can lead to analytical errors during analysis of the catalyst samples.

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